

Curable resin composition, coating composition, coating method and coated article

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Abstract

PCT No. PCT/JP95/00757 Sec. 371 Date Dec. 3, 1996 Sec. 102(e) Date Dec. 3, 1996 PCT Filed Apr. 18, 1995 PCT Pub. No. WO95/28452 PCT Pub. Date Oct. 26, 1995 The curable resin composition of this invention provides for a coating film having a high quality appearance, high acid resistance, mar resistance and further an excellent adhesive property and also can be provided with a high-solid feature. The coating composition obtainable with the curable resin composition of this invention can be provided with an excellent NSR-ability and can be advantageously used for automotive parts and exterior building materials, among other uses.

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(54) Title: CURABLE RESIN COMPOSITION, COATING COMPOSITION, COATING METHOD AND COATED ARTICLE		
(57) Abstract <p>The present invention provides a practical curable resin composition having an improved storage stability, mar resistance, acid resistance and an excellent appearance and meeting the high solid-requirement with NSR-ability which comprises 5 to 70 weight % of a polymer containing free and esterified carboxyl groups and having an acid value of 50 to 300 (mgKOH/g) (1e), 1 to 70 weight % of a hydroxyl group- and epoxy group-containing polymer having an epoxy equivalent of 200 to 1000, a hydroxyl equivalent of 250 to 1500 (2d), 1 to 45 weight % of an alkoxyl group-containing silicone polymer having an alkoxyl equivalent of 50 to 1500 and an epoxy equivalent of 100 to 1500 (3a), and 1 to 70 weight % of a polyester resin having a hydroxyl value of not greater than 300 (mgKOH/g), an acid value of 30 to 400 (mgKOH/g) and a molecular weight of 400 to 6000 (4a).</p>		

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SPECIFICATION

CURABLE RESIN COMPOSITION, COATING COMPOSITION,
COATING METHOD AND COATED ARTICLE

FIELD OF THE INVENTION

The present invention relates to a curable resin composition capable of forming a coating film of excellent quality in terms of acid resistance, mar resistance and appearance and which composition has an excellent property in storage stability and NSR-ability (defined and explained later), therefore, finding application in the fields of automotive top coatings, coil coatings, household electrical appliances, plastics and electrical materials, among other uses, and to a coating composition, a method of forming a coating film, and a coated article each as obtainable or implementable using said curable resin composition.

PRIOR ART

Automotive top coatings and a variety of coatings dedicated to the same purpose are required to possess a function to provide an aesthetic appearance and prolong the life of the car by evading damages due to winds and rains, stones, muds and dust by constituting the outermost layer of the coating structure inclusive of the primer and intermediate coating layers on the body of a car or the like and, therefore, must provide a film with high mar resistance and good appearance. The resin compositions used in such coatings are so designed that they will show viscosities before coating within a certain range that facilitates coating and, after application, may be easily cured to provide necessary resistance and appearance, that is to say they may exhibit a long storage stability and the optimum curability.

The conventional curing system for such automotive top coatings is an aminoplast curing agent such as a melamine

1 resin which reacts with the hydroxyl groups of a hydroxyl
group-containing polymer to achieve curing. However, the
above curing system is unsatisfactory in acid resistance and
the coating film obtained is liable to develop defects owing
5 to acidic rains which have recently been a major problem. The
defects are generally attributed to the triazine nucleus of
the melamine resin and no improvement in acid resistance
could be realized unless the use of melamine resin was avoided
or restricted to a sufficiently low level to avoid said
10 defects.

As a curing system not using a melamine resin, a method
employing a polyisocyanate compound is known but the toxicity
problem associated with the isocyanate has not been resolved.
Therefore, a curable resin composition of high nonvolatile
15 content comprising a polyoxide of low molecular weight, a
hydroxyl group-containing polyfunctional substance of low
molecular weight, a curing agent essentially comprising an
anhydride, and an acid catalyst was proposed (Japanese Kokai
Publication Sho-63-84674). However, this composition was
20 found to have the disadvantage that because its ingredients
are so reactive to each other that it cannot be stored in one
package, presenting a storage stability problem.

In view of the above state of the art, a technology
employing both (1) a half-esterified copolymer and (2) an
25 epoxy group- and hydroxyl group-containing compound in a
defined ratio to overcome the above-mentioned disadvantage
was disclosed (Japanese Patent Application Hei-2-91299). This
composition provided high acid resistance to overcome the
above disadvantage but was inadequate in mar resistance.

30 In view of the above problem, a technology was proposed
in which, in addition to the use of both (1) a half-esterified
(inclusive of half-thioesterified and half-amidated)
copolymer and (2) an epoxy group- and hydroxyl group-containing
compound, (3) at least one member selected from among an
35 acrylic polymer, a fluorine-containing copolymer and a

1 polyester resin, and (4) a melamine resin are used to provide
a composition according to a well-considered formula to
thereby overcome the above-mentioned disadvantage (Japanese
Kokai Publication Hei-4-363374). Although it contains a
5 melamine resin, this composition satisfies the acid
resistance requirement to a certain extent and provides good
mar resistance.

In the above technologies, the curing systems used
essentially require sufficiently high functional group
10 concentrations, so that the inevitable high viscosities
called for fair amounts of solvents. As such, these
technologies are unsuitable for production in areas where
regulations for environmental protection such as control over
VOC (volatile organic compounds) are in force and, moreover,
15 are deterrents to control of atmospheric pollution.
Therefore, even in the field of high-solid compositions, a
demand was felt for provision of a composition improved in
the above aspect.

Under the circumstances, as the result of research into a
20 high-solid resin composition satisfying the above performance
requirements, a technology was disclosed in which, in
addition to the use of both (1) a half-esterified copolymer
and (2) an epoxy group- and hydroxyl group-containing
compound, (3) a hydroxyl group- and carboxyl group-containing
25 silicone polymer is used to constitute a composition
according to a defined formula to thereby overcome the above
disadvantages (Japanese Patent Application Hei-5-224239).

The above technology adopts an acid anhydride curing
system and meets both the acid resistance and high-solid
30 requirements but does not satisfy more sophisticated
appearance and mar resistance requirements. Then, it was
discovered that the above disadvantages can be obviated by a
technology such that, in addition to the use of (1) a half-
esterified copolymer, (2) an epoxy group- and hydroxyl group-
35 containing polymer and (3) a hydroxyl group- and carboxyl

1 group-containing silicone polymer, (4) at least one pigment-
dispersing resin selected from among alkyd resin, polyester
resin, and basic substance-modified products of them, (5) a
pigment, and (6) an aminoplast curing agent (melamine resin)
5 are used to constitute a composition according to a defined
formulation and accordingly a Letters Patent was applied for
(Japanese Patent Application Hei-5-303849).

It will be obvious from the process of development of the
above technologies that in the effort to improve resin
10 compositions for coatings such as automotive top coatings,
addition of an aminoplast curing agent was first contemplated
in an attempt to insure a sufficiently long storage stability
and optimal curability and a subsequent endeavor to find a
new curing system over coming the drawback of consequently
15 reduced acid resistance resulted in a resin composition
comprising both a half-esterified copolymer and an epoxy
group- and hydroxyl group-containing polymer and not
containing an aminoplast curing agent, which was followed, in
the course of research for developing a high-solid coating,
20 by the idea of employing a silicone polymer having both
hydroxyl and carboxyl groups.

However, because the silicone polymer used in the above
technology is a silicone polymer provided with both carboxyl
and hydroxyl functions through reaction of the hydroxyl group
25 of a silicone polymer with an acid anhydride group, it has the
disadvantage of poor curability due to an insufficient number
of functional groups, with the result that when it is used in
a coating composition, the glass transition temperature (T_g)
cannot be increased. This disadvantage can be overcome by
30 incorporating a limited amount of an aminoplast curing agent
for improved curability but this practice inevitably entails a
certain decrease in the acid resistance which is necessary
for withstanding the influence of acidic rains.

The inventors did further research with the object of
35 providing an entirely new curable resin composition which

1 would show good curability essentially without the aid of an
aminoplast curing agent to provide a film with excellent acid
resistance, mar resistance and appearance and even having a
sufficient high-solid feature. They arrived at the finding
5 that the above-mentioned problems can be solved by compounding
the two basal components, namely (1) a half-esterified
copolymer and (2) an epoxy group- and hydroxyl group-
containing polymer, with (3) an epoxy group- and/or alkoxyl
group-containing silicone polymer as a third component and
10 accordingly filed a patent application. The above new curable
resin composition was sufficient to meet the high-solid
requirement and, at the same time, offered especially high
acid resistance and mar resistance.

Meanwhile, in the coating of a car body in the automotive
15 production line, for instance, it is common practice to
utilize the two-coat one-bake process which comprises coating
the substrate with a base coating composition comprising a
curable resin composition, then applying a clear coat thereon,
and baking the two coats at a time or the two-coat two-bake
20 process comprising two coating steps each followed by baking.
In either of such coating processes in the automotive
production line, defective coating takes place at times and on
every such occasion the necessary correction is made by a
non-sand recoating process which comprises applying a fresh
25 base coat on top of the baked clear coat, then applying a
fresh clear coat thereon and baking the two coats together.

Because the non-sand recoating process mentioned above
has much to do with an acceptable quality of car coating, a
demand for a coating composition having characteristics
30 suitable for non-sand recoating (briefly, NSR-ability) has
become demanded.

The base coating for the non-sand recoating process is
applied onto the clear coat previously applied and baked and,
therefore, unless it has a sufficiently high adhesive property,
35 peeling between the clear coat and the new base coat tends to

1 occur with the progress of time. And in order that the above
NSR-ability may be implemented, adhesive property to the clear
coat must be sufficiently increased.

5 The above-mentioned new curable resin composition for
satisfying the high solid requirement was designed to solve
the problem by compounding an epoxy group- and alkoxyl
group-containing silicone polymer. However, silicone polymers
are generally of low polarity and poor in compatibility and,
therefore, when a coating composition containing such a
10 polymer is applied to a substrate, the polymer tends to be
preferentially distributed in the superficial layer of the
coat, thus being a factor in the aging of adhesive property.
Moreover, the silicone polymer can also be a cause for a
decreased storage stability.

15 Furthermore, the silicone polymer is generally
comparatively expensive. When compared with the current
melamine high-solid coating, the use of the silicone polymer
alongside the polymer containing free and esterified carboxyl
groups and an epoxy group- and alkoxyl group-containing
20 silicone polymer is evidently disadvantageous from the
viewpoint of cost for the coating of regular-grade cars which
have to be inexpensive, although it offers a great merit for
the coating of deluxe cars.

25 Under the circumstances, the present invention has for
its object to provide an inexpensive and practical curable
resin composition with an improved storage stability, meeting
the high solid requirement without deterioration in mar
resistance, acid resistance and appearance and, in addition,
possessing said NSR-ability.

30 In view of the above state of the art, the present
invention has for its object to provide quite a new curable
resin composition which exhibits good curability essentially
without the aid of an aminoplast curing agent and, in
addition, has a fully high-solid characteristic.

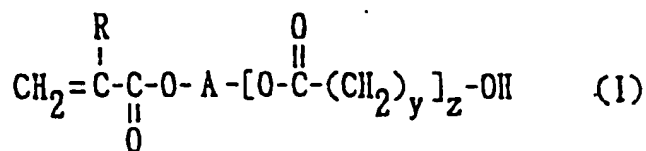
1 SUMMARY OF THE INVENTION

The gist of the present invention resides in the technology that a curable resin composition is provided by using

5 5 to 70 weight % of a polymer containing free and esterified carboxyl groups and having an acid value of 50 to 300 (mgKOH/g) and a number average molecular weight of 1500 to 8000 (1e) as obtainable by reacting an acid anhydride group-containing polymer (1c), which is obtainable by
 10 copolymerizing 10 to 40 weight % of an acid anhydride group-containing ethylenically unsaturated monomer (1a) with 90 to 60 weight % of a copolymerizable other ethylenically unsaturated monomer (1b), with a monohydric alcohol of 1 to 12 carbon atoms (1d) in the ratio (the number of mols of acid anhydride group in acid anhydride-containing polymer (1c)) /
 15 (the number of mols of hydroxyl group in monohydric alcohol (1d)) of 1/10 to 1/1,

1 to 70 weight % of a hydroxyl group- and epoxy group-containing polymer having an epoxy equivalent of 200 to 1000,
 20 a hydroxyl equivalent of 250 to 1500 and a number average molecular weight of 1500 to 8000 (2d) as obtainable by copolymerizing 5 to 60 weight % of a hydroxylalkyl (meth)acrylate monomer (2a) of the general formula (I):

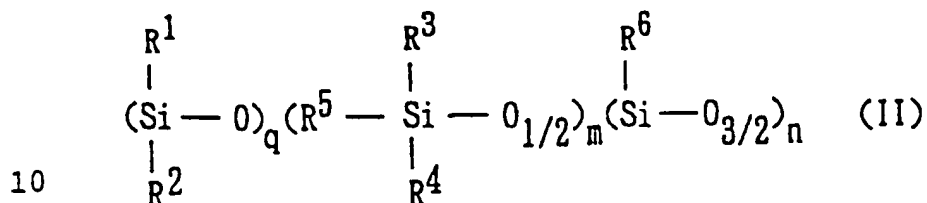
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30 (wherein R represents hydrogen or methyl; A represents a straight-chain or branched alkylene group of 2 to 8 carbon atoms; y represents a whole number of 3 to 7; z represents a whole number of 0 to 4) with 10 to 60 weight % of an epoxy group-containing ethylenically unsaturated monomer (2b) and 0
 35 to 85 weight % of an ethylenically unsaturated monomer (2c)

1 copolymerizable therewith,

1 to 45 weight % of an epoxy group- and/or alkoxyl group-
containing silicone polymer having an alkoxyl equivalent of 50
to 1500 and an epoxy equivalent of 100 to 1500 (3a) of the
5 general formula (II):



(wherein R¹, R², R³, R⁴, R⁵, and R⁶ are the same or different
and each represents alkyl of 1 to 10 carbon atoms, phenyl,
phenethyl, alkoxyl of 1 to 5 carbon atoms, R'-Si(OR'),,
15 R'-Si(OR')₂CH₃, R'-Si(OR')(CH₃)₂, or R'-Y; R' represents a
straight-chain or branched alkylene group which may have an
ether bond and/or an ester bond; R' represents alkyl of 1 to
5 carbon atoms; Y represents an epoxy group-containing acyclic
or cyclic hydrocarbon residue; q represents a whole number of
20 1 to 20, m represents a whole number of 0 to 4, n represents
a whole number of 0 to 2; the order of the parenthesized
groups occurring in q, m and n repetitions is random and not
restricted to the formula shown), and

1 to 70 weight % of a polyester resin having a hydroxyl
25 value of not greater than 300 (mgKOH/g), an acid value of 30
to 400 (mgKOH/g) and a number average molecular weight of 400
to 6000 (4a).

In another aspect thereof, the gist of the present
invention resides in the technology that a curable resin
30 composition is provided by using 5 to 70 weight % of a
polymer containing free and esterified carboxyl groups and
having an acid value of 50 to 300 (mgKOH/g) and a number
average molecular weight of 1500 to 8000 (1e),

1 to 70 weight % of a hydroxyl group- and epoxy group-
35 containing polymer having an epoxy equivalent of 200 to 1000,

1 a hydroxyl equivalent of 250 to 1500 and a number average
molecular weight of 1500 to 8000 (2d),

1 to 50 weight % of an epoxy group- and/or alkoxyl group-
containing silicone polymer having an alkoxyl equivalent of 50
5 to 1500 and an epoxy equivalent of 100 to 1500 (3a),

1 to 60 weight % of a polyester resin having a hydroxyl
value of 50 to 400 (mgKOH/g), an acid value of not greater
than 30 (mgKOH/g) and a number average molecular weight of 400
to 6000 (5a), and

10 1 to 40 weight % of an aminoplast curing agent (6a).

The compounding percentages of (1e), (2d), (3a), (4a),
(5a) and (6a) are based on the nonvolatile matter in the above
composition, and the proportions of the monomers for said
components (1e) and (2d) are based on the total amount of
15 monomers constituting each component.

The present invention is further concerned with a coating
composition containing said curable resin composition, a
method of forming a coating film using said coating
composition, and a coated article as obtained using said
20 coating composition.

DETAILED DESCRIPTION OF THE INVENTION

The first component constituting the curable resin
composition of the present invention is a polymer (1e)
25 containing both free and esterified carboxyl groups and
having an acid value of 50 to 300 (mgKOH/g). This polymer
(1e) can be prepared by reacting an acid anhydride group-
containing polymer (1c) with a monohydric alcohol (1d) of 1
to 12 carbon atoms for half-esterification.

30 The acid anhydride group-containing polymer (1c)
mentioned above can be prepared by copolymerizing 10 to 40
weight %, preferably 15 to 30 weight %, of an acid anhydride
group-containing ethylenically unsaturated monomer (1a) with
60 to 90 weight %, preferably 70 to 85 weight %, of a
35 copolymerizable other ethylenically unsaturated monomer (1b).

1 When the proportion of said acid anhydride group-
containing ethylenically unsaturated monomer (1a) is less than
10 weight %, no sufficient curability can be obtained, while
the use of an excess over 40 weight % results in an
5 excessively hard, brittle coat with inadequate weather
resistance.

 The acid anhydride group-containing ethylenically
unsaturated monomer (1a) mentioned above is not particularly
limited in kind only if it is an ethylenically unsaturated
10 monomer containing a carboxylic anhydride group and includes
itaconic anhydride, maleic anhydride and citraconic anhydride,
among others.

 The other ethylenically unsaturated monomer (1b)
copolymerizable with said acid anhydride group-containing
15 ethylenically unsaturated monomer (1a) is not particularly
limited in kind, either, only if it does not adversely affect
the acid anhydride group. Thus, monomers of 2 to 15 carbon
atoms containing one ethylenically unsaturated bond are
preferred and those of 3 to 12 carbon atoms are still more
20 preferred. Moreover, the use of two or more different
monomers particularly contributes to enhanced compatibility
of resins.

 The free carboxyl groups of the polymer (1e) containing
both free and esterified carboxyl groups can be derived from
25 the use of a carboxyl group-containing monomer (1b') as said
copolymerizable other ethylenically unsaturated monomer (1b)
for copolymerization with said (1a), followed by reaction of
the resulting polymer (1c) with the monohydric alcohol (1d)
as will be described hereinafter. In this case, said
30 carboxyl group-containing monomer (1b') is used only in an
amount providing for an acid value within the range of 50 to
300 (mgKOH/g) for (1e). The kind of said carboxyl group-
containing monomer (1b') is not particularly limited. Thus,
acrylic acid and methacrylic acid, among others, can be used
35 and one or more of them can be used in combination.

1 1

1 The copolymerizable other ethylenically unsaturated
monomer (1b) mentioned above further includes, in addition to
said monomer (1b²), such other monomers as styrene and its
derivatives, e.g. α -methylstyrene, para-t-butylstyrene, etc.;
5 (meth)acrylic esters such as methyl (meth)acrylate, ethyl
(meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate,
i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl
(meth)acrylate, lauryl (meth)acrylate, cyclohexyl
(meth)acrylate, isobornyl (meth)acrylate, etc.; and Veova-9,
10 Veova-10, etc. (manufactured by Shell). When styrene or a
styrene derivative is used for said copolymerizable other
ethylenically unsaturated monomer (1b), it is used preferably
within the range of 5 to 40 weight %. If the limit of 40
weight % is exceeded, weather resistance is adversely affected.

15 The copolymerization reaction between said acid anhydride
group-containing ethylenically unsaturated monomer (1a) and
said copolymerizable other monomer (1b) can be carried out in
the known manner, for example by a radical polymerization
method in solution, either at atmospheric pressure or at
20 elevated pressure and a polymerization temperature of 100 to
200°C for a polymerization time of 3 to 8 hours. As the
polymerization initiator, an azo type initiator or a peroxide
type initiator can be advantageously employed and its
preferred amount is 0.5 to 15 parts by weight relative to 100
25 parts by weight of the total monomer. To the above monomer
composition, other additives such as a chain transfer agent
can be added.

 The preferred number average molecular weight of the acid
anhydride group-containing polymer (1c) obtained by the above
30 copolymerization reaction is 1500 to 8000. If the number
average molecular weight is less than 1500, the curability of
the curable resin composition will be inadequate. If it
exceeds 8000, the polymer viscosity is increased to interfere
with the manufacture of a high-solid coating composition. The
35 more preferred molecular weight range is 1800 to 4000. These

1 molecular weight values can be determined by, for example,
gel permeation chromatography (GPC).

The above-mentioned acid anhydride group-containing
polymer (1c) preferably contains at least 2 acid anhydride
5 groups per molecule and more preferably contains 2 to 15 acid
anhydride groups per molecule. If the number of acid
anhydride groups is less than 2, no sufficient curability can
be expected. If it is greater than 15, the cured product will
be too hard and brittle and lacking in adequate weather
10 resistance.

As the above acid anhydride group-containing polymer (1c)
is reacted with the monohydric alcohol (1d), it is half-
esterified so that a polymer containing both free and
esterified carboxyl groups (1e) can be obtained. The end
15 point of half-esterification reaction can be confirmed from
substantial disappearance of the absorption of acid anhydride
groups at about 1785 cm^{-1} on the infrared absorption
spectrum.

The monohydric alcohol (1d) mentioned above is a low
20 molecular weight compound containing 1 to 12 carbon atoms and
preferably a compound of 1 to 8 carbon atoms, Where the
carbon number is 1 to 12, the low molecular weight monohydric
alcohol (1d) is vaporized on heating to favor the
regeneration of the acid anhydride group.

25 The monohydric alcohol (1d) that can be used includes a
variety of alcohols of low molecular weight such as methanol,
ethanol, propanol, butanol, methylcellosolve (trademark),
ethylcellosolve (trademark), dimethylaminoethanol,
diethylaminoethanol, acetol, allyl alcohol, propargyl alcohol,
30 furfuryl alcohol and so on. Among them, acetol, allyl
alcohol, propargyl alcohol, methanol and furfuryl alcohol are
preferred.

The ratio of said acid anhydride group-containing polymer
(1c) and monohydric alcohol (1d) for use in the above-
35 mentioned half-esterification reaction is 1/10 to 1/1 in

1 terms of the ratio of the number of mols of acid anhydride
group in (1c) to the number of mols of hydroxyl group in (1d).
If the ratio is less than 1/10, the excess monohydric alcohol
tends to cause popping at the curing step. On the other hand,
5 if the ratio exceeds 1/1, the unreacted acid anhydride groups
detract from the storage stability. The more preferred ratio
is 1/8 to 1/1.1.

The above half-esterification reaction can be carried out
in the conventional manner at a temperature from room
10 temperature to 120°C.

The polymer (1e) containing free and esterified carboxyl
groups and having an acid value of 50 to 300 (mgKOH/g) as
obtained by the above reaction is used as a first component of
the curable resin composition of the present invention. If
15 the acid value is less than 50, curability will be poor. If
300 is exceeded, excessive hardness and decreases in weather
resistance will be encountered. Neither of such polymers can
be used for the purposes of the present invention. The range
of 75 to 200 is preferred.

20 The second component of the curable resin composition of
this invention is a hydroxyl group- and epoxy group-containing
polymer (2d). The epoxy equivalent of the polymer (2d) is
200 to 1000 and the hydroxyl equivalent thereof is 250 to 1500.
If the epoxy equivalent is less than 200, excessive hardening
25 results in a brittle film. On the other hand, if 1000 is
exceeded, the curability of the curable resin composition
will become insufficient. Moreover, if the hydroxyl
equivalent is less than 250, the water resistance of the cured
coat will be insufficient. On the other hand, if 1500 is
30 exceeded, only insufficient curability can be obtained. The
epoxy equivalent is preferably 250 to 800 and, for still
better results, 300 to 700. The hydroxyl equivalent is
preferably 300 to 1200 and, for still better results, 400 to
1000.

35 The above polymer (2d) containing hydroxyl and epoxy

1 groups can be obtained by copolymerizing 5 to 60 weight %, preferably 15 to 40 weight %, of a hydroxyalkyl (meth)acrylate of general formula (I) with 10 to 60 weight %, preferably 15 to 50 weight %, of an epoxy group-containing
5 ethylenically unsaturated monomer (2b), and where necessary, further with 0 to 85 weight %, preferably 10 to 70 weight %, of one or more other ethylenically unsaturated monomers (2c).

If the proportion of said hydroxyalkyl (meth)acrylate (2a) is less than 5 weight %, no sufficient curability can be
10 obtained. On the other hand, if 60 weight % is exceeded, compatibility is sacrificed so that the reaction cannot proceed to a sufficient extent. Moreover, if the proportion of said epoxy group-containing ethylenically unsaturated monomer (2b) is less than 10 weight %, curability will be
15 insufficient. If 60 weight % is exceeded, excessive hardening and poor weather resistance are encountered.

The carbon number of the hydroxyalkyl moiety of said hydroxyalkyl (meth)acrylate monomer (2a) is 2 to 20 and preferably 2 to 10. If the carbon number is too large, the
20 inter-crosslink molecular weight will be undesirably too large.

The hydroxyalkyl (meth)acrylate monomer (2a) that can be used includes but is not limited to 2-hydroxy ethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, etc. and
25 reaction products of these monomers with ϵ -caprolactone. These compounds are available from commercial sources, and "Placel FM1" and "Placel FA1" (both manufactured by Daicel Chemical Industries) can be mentioned. Moreover, such compounds can be prepared by esterifying (meth)acrylic acid
30 with a large excess of a diol compound.

The epoxy group-containing ethylenically unsaturated monomer (2b) mentioned above includes glycidyl (meth)acrylate, 2-methylglycidyl (meth)acrylate, 3,4-epoxycyclohexanylethyl (meth)acrylate and so on.

35 The copolymerizable ethylenically unsaturated monomer

1 (2c) mentioned above includes, among others, these compounds
mentioned specifically as examples of said other ethylenically
unsaturated monomer (1b) copolymerizable with acid anhydride
group-containing ethylenically unsaturated monomer (1a).

5 The copolymerization reaction involving said hydroxyalkyl
(meth)acrylate monomer (2a), epoxy group-containing
ethylenically unsaturated monomer (2b) and copolymerizable
ethylenically unsaturated monomer (2c) can be carried out in
the known manner, for example by the radical polymerization
10 method in solution, at atmospheric pressure or at elevated
pressure and a polymerization temperature of 100 to 200°C for
a polymerization time of 3 to 8 hours. As the polymerization
initiator, a conventional initiator of the azo type or of the
peroxide type can be successfully employed. The above
15 polymerization initiator is used preferably in a proportion
of 0.5 to 15 weight % based on the total monomer in the
reaction system. Additives such as a chain transfer agent
can also be added to said monomer composition.

The number average molecular weight of the hydroxyl
20 group- and epoxy group-containing polymer (2d) as obtained by
the above copolymerization reaction is preferably 1500 to
8000 and, for still better results, 1600 to 4000. If the
number average molecular weight exceeds 8000, the polymer
viscosity becomes increased to interfere with preparation of
25 a high-solid coating composition. On the other hand, if the
molecular weight is less than 1500, the curability of the
curable resin composition will be insufficient.

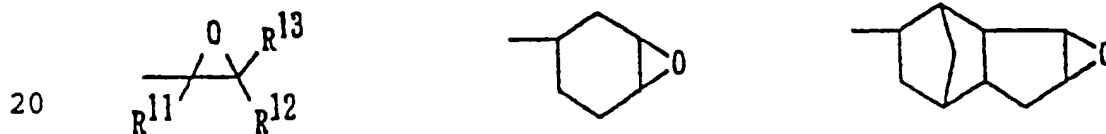
The third component of the curable resin composition of
the present invention is a silicone polymer containing epoxy
30 and/or alkoxy groups (3a). This polymer is represented by
general formula (II).

The epoxy group-containing silicone polymer includes "NUC
Silicone" series manufactured by Nippon Unicar Co., among
others. The alkoxy group-containing silicone polymer
35 includes "KC-89S" manufactured by Shin-Etsu Chemical

1 Industries, among others. The silicone polymer containing
 epoxy and alkoxyl groups includes "MKC Silicate MSEP2" series
 manufactured by Mitsubishi Kasei Corporation and "NUC
 Silicone" series manufactured by Nippon Unicar Co., among
 5 others.

The technology of producing a silicone polymer containing
 epoxy and/or alkoxyl groups is described in Synopsis of 1990
 Symposium for the Chemistry of Organo silicon Materials,
 pp. 29 to 30.

10 The epoxy groups in said silicone polymer (3a) exist in
 intermediate or terminal positions of the acyclic or cyclic
 hydrocarbon chains. In silicone polymer (3a), the epoxy
 group-containing acyclic or cyclic hydrocarbon designated by Y
 may, for example, be represented by any of the following
 15 formulas.



25 In the above formulas, R¹¹, R¹² and R¹³ each represents a
 hydrocarbon of 0 to 4 carbon atoms.

In this specification, "epoxy equivalent" means the
 number of grams of a compound containing one gram equivalent
 of epoxy group, "alkoxyl equivalent" means the number of grams
 of a compound containing one gram equivalent of alkoxyl group,
 30 and "hydroxyl equivalent" means the number of grams of a
 compound containing one gram equivalent of hydroxyl group.

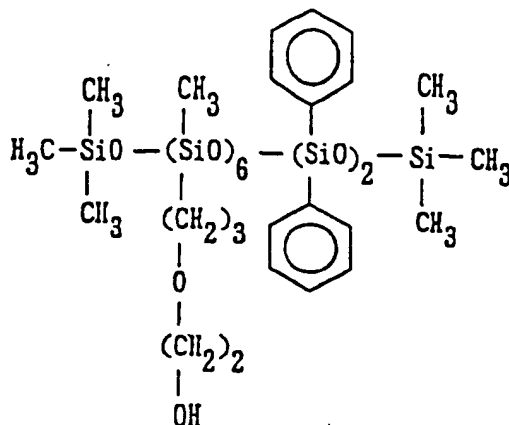
The epoxy equivalent of the silicone polymer (3a)
 according to the present invention is 100 to 1500 and the
 alkoxyl equivalent thereof is 50 to 1500. If the epoxy
 35 equivalent is less than 100, the storage stability of the

1 coating is sacrificed. If it exceeds 1500, poor curability
will result. The preferred range of epoxy equivalent is 140
to 1000 and the more desirable range is 180 to 700. The
5 preferred range of alkoxy equivalent is 60 to 800 and the
more desirable range is 80 to 500.

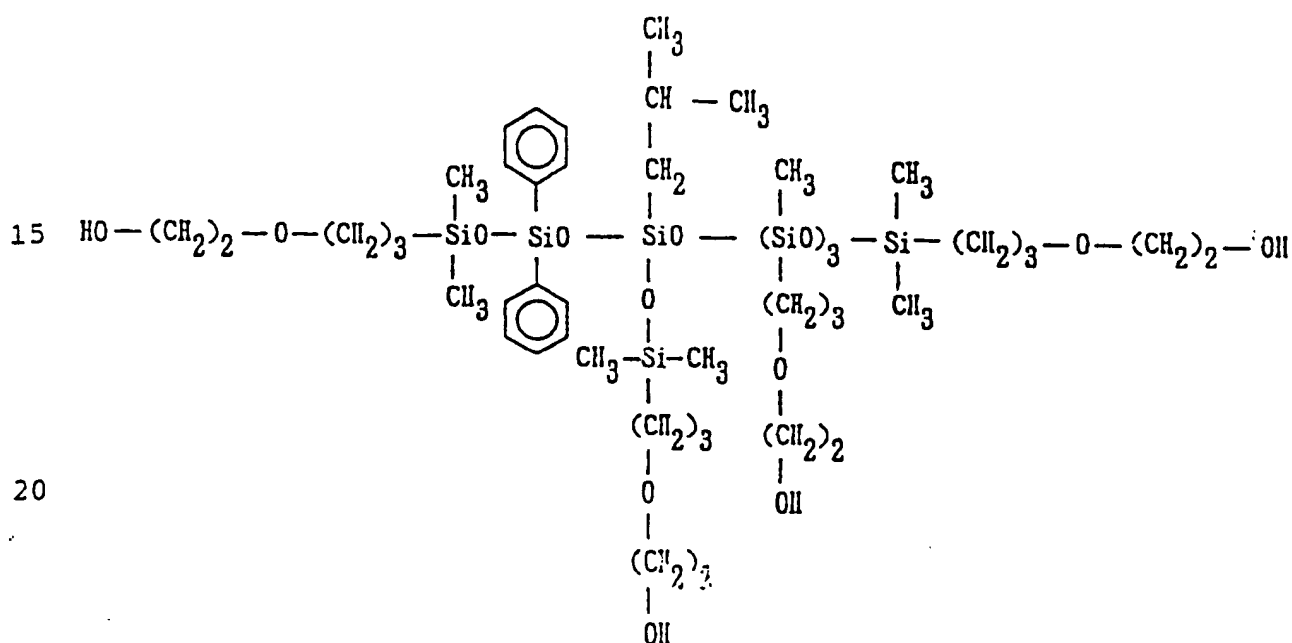
In the present invention, a hydroxyl group- and carboxyl
group-containing silicone polymer (3b) can be admixed along
with said epoxy- group and/or alkoxy group-containing
silicone polymer (3a). The silicone polymer (3b) containing
10 hydroxyl and carboxyl groups can be obtained by subjecting a
hydroxyl group-containing silicone polymer (3c) and an acid
anhydride group-containing compound (3d) to half-
esterification reaction.

The hydroxyl group-containing silicone polymer (3b)
15 mentioned above is available from commercial sources, and
"KR-2001" manufactured by Shin-Etsu Silicone Co. and "NUC-
Silicone" series manufactured by Nippon Unicar, the chemical
formulas of which are presented below, can be mentioned as
examples.

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25 The hydroxyl group-containing silicone polymer (3c)
mentioned above preferably contains an average of 3 to 12
hydroxyl groups per molecule. If the average number of
hydroxyl groups contained per molecule of said hydroxyl
group-containing silicone polymer (3c) is less than 3,
30 curability is insufficient. If 12 is exceeded, viscosity is
increased so that it is difficult to increase the
concentration of nonvolatile matter of the coating
composition.

35 The acid anhydride group-containing compound (3d) is not particularly limited in kind only if it reacts with a hydroxyl

35

1 group under ordinary conditions, e.g. room temperature to
120°C and atmospheric pressure, to generate a carboxyl
function. The use of an acid anhydride group-containing
compound having a saturated or unsaturated cyclic group of 8
5 to 12 carbon atoms is preferred because it contributes to
enhanced compatibility of resins.

As such, said acid anhydride group-containing compound
(3d) includes hexahydrophthalic anhydride, phthalic anhydride,
4-methylhexahydrophthalic anhydride, tetrahydrophthalic
10 anhydride and trimellitic anhydride, among others.

The half-esterification reaction between said hydroxyl
group-containing silicone polymer (3c) and said acid anhydride
group-containing compound (3d) can be conducted in the
conventional manner, for example at a temperature of room
15 temperature to 120°C for 30 minutes to 8 hours. If the
reaction is conducted at a temperature exceeding 120°C over a
long time, polyesterification reaction takes place to yield a
silicone polyester of high molecular weight. Such silicone
polyesters have few functional groups and high viscosities so
20 that they are not suited for use in the present invention.

The fourth component of the curable resin composition of
the present invention is a polyester resin (4a). This
polyester resin is produced by condensation reaction
between a polyhydric alcohol and an ordinary acid or acid
25 anhydride.

The polyhydric alcohol mentioned above includes ethylene
glycol, propylene glycol, 1,3-butylene glycol, 1,6-hexanediol,
diethylene glycol, dipropylene glycol, neopentyl glycol,
triethylene glycol, bisphenol A hydrate, phenol
30 dihydroxypropyl ether, glycerin, trimethylolethane,
trimethylolpropane, pentaerythritol, and dipentaerythritol,
among others.

The acid or acid anhydride forming an ester bond with
said polyhydric alcohol includes but is not limited to
35 dibasic acids such as phthalic acid, isophthalic acid,

1 terephthalic acid, succinic acid, adipic acid, azelaic acid,
sebacic acid, tetrahydrophthalic acid, hexahydrophthalic acid,
maleic acid, fumaric acid, etc. and acid anhydrides such as
succinic anhydride, phthalic anhydride, tetrahydrophthalic
5 anhydride, hexahydrophthalic anhydride,
phthalic himic anhydride, trimellitic anhydride,
methylcyclohexenetricarboxylic anhydride, pyromellitic
anhydride and so on. Aside from the above compounds, if
necessary, castor oil, coconut oil, linseed oil, palm-kernel
10 oil, safflower oil, soybean oil, tung oil, tall oil,
dehydrated castor oil, etc. can also be used for modifying
said polyhydric alcohol.

In the present invention, the proportion of a straight-
chain fatty acid containing more than 12 carbon atoms is
15 preferably not more than 25 weight % based on the total
weight of the monomers constituting the polyester resin. If
it exceeds 25 weight %, the adhesion between the underling
surface and the coat formed from the coating composition of
the present invention is decreased so that the object of the
20 invention cannot be accomplished. The range of 1 to 20
weight % is still more preferred and the range of 1 to 15
weight % is most desirable. The oils mentioned above are rich
in acids containing not less than 12 carbon atoms and since
the majority of acids occurring in coconut oil and
25 palm-kernel oil, for instance, contain not less 12 carbon
atoms, the so-called oil-free polyester resin is particularly
preferred for the present invention.

The hydroxyl group present in said polyester resin may be
chain-extended using a lactone chain for the purpose of
30 softening the resin. Among the preferred chain-extender
lactone can be mentioned γ -butyrolactone and
 ϵ -caprolactone.

Moreover, an epoxy group-containing synthetic fatty acid
derivative such as Cardura E-10 (manufactured by Shell) may
35 also be employed.

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1 The hydroxyl value of said polyester resin (4a) is not
greater than 300 (mgKOH/g) and preferably not greater than 250
(mgKOH/g). For still better results, not greater than 220
(mgKOH/g). If the hydroxyl value is greater than 300, water
5 resistance is insufficient.

 The acid value is 30 to 400 (mgKOH/g) and preferably 50
to 350 (mgKOH/g). For still better results, 60 to 200
(mgKOH/g). If it is under 30, curability is insufficient. If
it exceeds 400, the storage stability and the weather
10 resistance of the coating is adversely affected.

 The number average molecular weight is 400 to 6000 and
preferably 500 to 4000. The range of 600 to 3000 is still
more preferred. If it is less than 400, water resistance is
decreased. If it exceeds 6000, a decrease in solid content is
15 inevitable.

 Thus, the curable resin composition of this invention is
produced by compounding 5 to 70 weight % of said polymer (1e)
containing free and esterified carboxyl groups, 1 to 70
weight % of a hydroxyl group- and epoxy group-containing
20 polymer (2d), 1 to 45 weight % of an epoxy group- and/or
alkoxyl group-containing silicone polymer (3a), and 1 to 70
weight % of a polyester resin (4a) as essential components.
The weight % values given above are percentages based on the
total solid matter of polymers (1e), (2d), (3a) and (4a). If
25 the proportions of polymers (1e) and (2d) deviate from the
above formulation ranges, curability is sacrificed. If the
proportion of silicone polymer (3a) is smaller than the above
formulation range, the concentration of solids cannot be
increased. If (3a) is used too much, the composition becomes
30 soft and suffers from insufficient cure. If the proportions
of polyester resin (4a) deviate from the above formulation
ranges, deterioration of weather resistance may be inevitable.

 The above compounding ratio is specifically determined in
such a manner that the molar ratio of the carboxyl group
35 contained in said polymer (1e) containing free and esterified

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1 carboxyl groups and said polyester resin (4a) to the epoxy
group contained in said polymer (2d) containing hydroxyl and
epoxy groups and said silicone polymer (3a) containing epoxy
and/or alkoxy groups, namely the (carboxyl group) / (epoxy
5 group) ratio, will be 1/1.6 to 1/0.6. In order that the
molar ratio may fall within the above range, the proportions
of said four components of the present invention are
respectively selected within the range of (1e) 5 to 70
weight %, the range of (2d) 1 to 70 weight %, the range of
10 (3a) 1 to 45 weight %, and the range of (4a) 1 to 70 weight %.
The preferred ranges are (1e) 10 to 50 weight %, (2d) 5 to 60
weight %, (3a) 5 to 43 weight %, and (4a) 5 to 50 weight %.
The more desirable ranges are (1e) 15 to 45 weight %, (2d) 7
to 55 weight %, (3a) 10 to 40 weight %, and (4a) 10 to 40
15 weight %. If the above ratio is smaller than 1/1.6, the
coating film undergoes yellowing. On the other hand, if the
ratio of 1/0.6 is exceeded, the curability of the product
resin composition is sacrificed. The above molar ratio is
more preferably 1/1.3 to 1/0.8. It should be understood that
20 when said silicone polymer (3b) containing hydroxyl and
carboxyl groups is used in addition to said (3a), said number
of moles of carboxyl group is the sum of numbers of moles of
carboxyl group contained in said (1e), (3b) and said (4a).

With respect to another aspect of the present invention,
25 a polyester resin (5a) is used as the fourth component and an
aminoplast curing agent (6a) is used as the fifth component
along with the first, the second and the third components
mentioned above. The polyester resin (5a) mentioned above is
produced by condensation reaction between a polyhydric alcohol
30 and an ordinary acid or acid anhydride.

As the polyhydric alcohol mentioned above, there may be
mentioned the ones described previously. As the acid or acid
anhydride forming an ester bond with said polyhydric alcohol
mentioned above, there may be mentioned the ones described
35 above.

1 The hydroxyl value of said polyester resin (5a) is 50 to
400 (mgKOH/g) and preferably 70 to 350 (mgKOH/g). If the
hydroxyl value is less than 50, curability is insufficient.
If it exceeds 400, water resistance is decreased.

5 The acid value is preferably not greater than 30
(mgKOH/g) and, for still better results, 1 to 25 (mgKOH/g).
If it exceeds 30, the storage stability of the coating is
adversely affected.

10 The number average molecular weight is 400 to 6000 and
preferably 500 to 4000. If it is less than 400, water
resistance is decreased. If it exceeds 6000, a decrease in
solid content is inevitable.

15 The fifth component of the curable resin composition of
another aspect of the present invention is an aminoplast
curing agent (6a).

20 The aminoplast curing agent (6a) mentioned above is used
for increasing the crosslink density and water resistance of
the curable resin composition of another aspect of the
present invention. The aminoplast curing agent can be any
ordinary one used in coatings and includes melamine resin,
benzoguanamine, benzoguanamine hydroxide, alcohol-modified
urea-formaldehyde adduct, and so on. These curing agents can
be used singly or in combination.

25 As said aminoplast curing agent, an etherified
melamine-fatty acid aldehyde adduct, particularly etherified
melamine-formaldehyde adduct, is preferred. The etherified
melamine resin is, for example, the resin in which the
hydrogen of the methylol group added to the amino group has
been substituted with an alkyl group. This alkyl group may
30 for example be methyl, ethyl, n-butyl or isobutyl.

35 The melamine resin of high etherification degree
requiring a strong acid catalyst is not satisfactory in
curability and cannot be used in another aspect of the present
invention. The average amount of alkyl ether group per
triazine ring is preferably not greater than 70%. The amount

1 of alkyl ether group as mentioned above is the average amount
in % of the alkyl ether groups actually added, with the case
in which all the hydrogen atoms of amino groups in the
melamine resin have been substituted with alkanols and all
5 the terminal hydroxyl groups have been substituted with
alkoxyl groups being taken as 100%. Since the number of amino
groups per triazine ring is 3, a value of not less than 50%
for alkyl ether groups indicates that an average of 3 or more
alkyl ether groups have been added per triazine ring. As
10 typical species of said melamine resin, Cymel 202, Cymel 327
(Mitsui-Cytec), Uvan 128, Uvan 20N-60 (Mitsui Toatsu Chemical),
and Super-Beckamine 13-548 (Dainippon Ink and Chemicals) can
be mentioned.

Thus, the curable resin composition of another aspect of
15 this invention is produced by compounding 5 to 70 weight % of
said polymer (1e) containing free and esterified carboxyl
groups, 1 to 70 weight % of a hydroxyl group- and epoxy group-
containing polymer (2d), 1 to 50 weight % of an epoxy group-
and/or alkoxyl group-containing silicone polymer (3a), 1 to
20 60 weight % of a polyester resin (5a), and 1 to 40 weight %
of an aminoplast curing agent (6a) as essential components.
The weight % values given above are percentages based on the
total solid matter of polymers (1e), (2d), (3a), (5a) and
(6a). If the proportions of polymers (1e) and (2d) deviate
25 from the above formulation ranges, curability is sacrificed.
If the proportion of silicone polymer (3a) is smaller than the
above formulation range, the concentration of solids cannot
be increased. If (3a) is used too much, the composition
becomes soft and suffers from insufficient cure.
30 If the proportions of polyester resin (5a) deviate from the
above formulation ranges, curability is sacrificed. If the
proportions of aminoplast curing agent (6a) deviate from the
above formulation ranges, deterioration of weather resistance
may be inevitable.

35 The above compounding ratio is specifically determined in

1 such a manner that the molar ratio of the carboxyl group
contained in said polymer (1e) containing free and esterified
carboxyl groups and said polyester resin (5a) to the epoxy
group contained in said polymer (2d) containing hydroxyl and
5 epoxy groups and said silicone polymer (3a) containing epoxy
and/or alkoxy groups, namely the (carboxyl group) / (epoxy
group) ratio, will be 1/1.6 to 1/0.6. In order that the
molar ratio may fall within the above range, the proportions
of said four components of the present invention are
10 respectively selected within the range of (1e) 5 to 70
weight %, the range of (2d) 1 to 70 weight %, the range of
(3a) 1 to 50 weight %, the range of (5a) 1 to 60 weight %,
and the range of (6a) 1 to 40 weight %. The preferred ranges
are (1e) 10 to 60 weight %, (2d) 5 to 60 weight %, (3a) 3 to
15 30 weight %, (5a) 5 to 40 weight %, and (6a) 3 to 30 weight %.
The more desirable ranges are (1e) 15 to 50 weight %, (2d) 8
to 50 weight %, (3a) 5 to 20 weight %, (5a) 8 to 35 weight %,
and (6a) 5 to 20 weight %. If the above ratio is smaller than
1/1.6, the coating film undergoes yellowing. On the other
20 hand, if the ratio of 1/0.6 is exceeded, the curability of
the product resin composition is sacrificed. The above molar
ratio is more preferably 1/1.3 to 1/0.8. It should be
understood that when said silicone polymer (3b) containing
hydroxyl and carboxyl groups is used in addition to said (3a),
25 said number of moles of carboxyl group is the sum of numbers
of moles of carboxyl group contained in said (1e), (3b) and
said (5a).

The weight ratio of said polyester resin (5a) to said
aminoplast curing agent (6a) is preferably 9/1 to 4/6. The
30 range of 6.5/3.5 to 4.5/5.5 is still more preferred, and the
range of 6/4 to 5/5 is most desirable. If this ratio exceeds
9/1, curability is sacrificed. If this ratio is below 4/6,
weather resistance is sacrificed due to the excessive hardness
of the coated film. Thus the weight ratio mentioned above is
35 limited within above-mentioned range.

1 The weight ratio of total of said (5a) and said (6a) to
total of said (1e), (2d) and (3a) is preferably 5/95 to 7/3.
The range of 7/93 to 6/4 is still more preferred, and the
range of 1/9 to 5/5 is most desirable. If this ratio is below
5 5/95, appearance is sacrificed. If this ratio exceeds 7/3,
acid resistance is sacrificed. Thus the weight ratio
mentioned above is limited within above-mentioned range.

 The nonvolatile matter (SVS) in the curable resin
composition of this invention is preferably not less than 40%
10 in terms of volume and more preferably not less than 45% on
the same basis. If the amount of nonvolatile matter is less
than the above level, the composition is not suitable for use
in the areas where regulations for solvent control are in
force.

15 The mechanism of cure of the curable resin composition of
this invention is now explained. First, on heating, the
carboxyl group and carboxylic ester group in (1e) react to
give an acid anhydride group within (1e), with liberation of
free monohydric alcohol. The monohydric alcohol so produced
20 is vaporized and removed from the reaction system. The acid
anhydride group generated in (1e) reacts with the hydroxyl
group of (2d) to form a crosslink and a free carboxyl group
is regenerated. This carboxyl group and the carboxyl group
initially present in (1e) and the carboxyl group contained in
25 (4a) or (5a) react with the epoxy groups in (2d) or, where
(3a) contains an epoxy group, with the epoxy groups of (2d)
and (3a) to form crosslinks.

 On the other hand, when (3a) contains alkoxy groups, the
alkoxy group of (3a) reacts with the hydroxyl group of (2d)
30 and the carboxyl group of (4a) or (5a) to form a crosslink.
The liberated monohydric alcohol is vaporized and removed
from the reaction system. The alkoxy group is hydrolyzed by
the water present in the reaction system to give a silanol
group and a monohydric alcohol. The monohydric alcohol thus
35 produced is evaporated and removed from the reaction system.

1 The silanol group formed in (3a) undergoes dehydrative
condensation with the hydroxyl group of (2d) and between
silanol groups to form crosslinks. The byproduct water is
vaporized and removed from the system. The silanol group
5 reacts with the alkoxyl group to form a crosslink with
elimination of alcohol. The alcohol thus liberated is
vaporized and removed from the system. In this manner, the
curable resin composition cures progressively as the result
of interaction of (1e), (2d), (3a) and (4a) or (5a).

10 It will be apparent from the above reactions that where
(3a) contains alkoxyl groups, the alkoxyl group invariably
exists in the form of an alkoxysilyl group.

In the curable resin composition of this invention, a
curing catalyst such as a quaternary ammonium salt which is
15 usually employed for an esterification reaction between an
acid and an epoxy compound can be incorporated. The curing
catalyst that can be employed includes benzyltriethylammonium
chloride, benzyltriethylammonium bromide, tetrabutylammonium
chloride, tetrabutylammonium bromide, tetrabutylammonium
20 salicylate, tetrabutylammonium glycolate, tetrabutylammonium
p-toluenesulfonate and so on. These catalysts can be used in
combination.

The preferred compounding amount of said catalyst is 0.1
to 5.0 weight % based on the solid matter of resin.

25 For the curable resin composition of the present
invention, a tin compound can be used as a catalyst in
combination with the above-mentioned curing catalyst as
disclosed in Japanese Kokai Publication Hei-2-151651 and
Japanese Kokai Publication Hei-2-279713.

30 The tin compound mentioned above includes dimethyltin
bis(methylmalate), dimethyltin bis(ethylmalate), dimethyltin
bis(butylmalate), dibutyltin bis(butylmalate), monobutyltin
bis(methylmalate), monobutyltin bis(ethylmalate), monobutyltin
bis(butylmalate), monomethyltin bis(butylmalate), etc. The
35 preferred compounding weight ratio of said curing catalyst

1 and said tin compound is 1/4 to 1/0.2.

For enhanced crosslinking density and improved water resistance of the curable resin composition of the present invention containing (1e), (2d), (3a) and (4a), an aminoplast
5 curing agent, a blocked isocyanate, etc. can also be employed. The aminoplast curing agent can be any ordinary one used in coatings and includes melamine resin, benzoguanamine, benzoguanamine hydroxide, alcohol-modified urea-formaldehyde adduct, and so on. These curing agents can be used singly or
10 in combination.

There is no particular limitation on the method for production of the curable resin composition of the present invention.

The coating composition of the present invention can be
15 provided by formulating the curable resin composition of the present invention in the conventional manner. As the solvent for use in the production of the coating composition of the present invention, organic solvents that are conventionally used in coatings or a mixture of such solvents can be employed.
20 Among such solvents may be mentioned aromatic hydrocarbon solvents such as toluene and xylene, aliphatic hydrocarbon solvents such as n-hexane and heptane, petroleum cracking fractions composed predominantly of aliphatic hydrocarbons and containing aromatic hydrocarbons, esters such as butyl
25 acetate, ethylene glycol diacetate, 2-ethoxyethyl acetate, etc., ketones such as methyl isobutyl ketone, and alcohols such as butyl alcohol.

For improved weather resistance of the coat formed from said coating composition, an ultraviolet absorber, e.g.
30 benzophenone derivatives, benzotriazole derivatives, etc., a hindered amine light stabilizer, a phenolic antioxidant, etc. can be added. Aside from the above additives, a rheology modifier (an agent for sag control) such as a particulate crosslinked resin, and a surface modifier for modulating the
35 appearance of the coat can also be added.

1 For adjusting the viscosity of said coating composition, among other purposes, an alcoholic solvent such as methanol, ethanol, propanol, butanol, etc., a hydrocarbon solvent, an ester solvent or the like can be used as the diluent.

5 For an increased storage stability of said coating composition, a hydrolyzable ester solvent such as trimethyl orthoformate, trimethyl orthoacetate, triethyl orthoacetate, etc. can also be added. The preferred level of addition of this solvent is 1 to 10 weight % relative to the paint.

10 The coating composition of the present invention can be applied by spray coating, brush coating, dip coating, roll coating, flow coating, rotary atomizing coating or other method.

15 For use of the coating composition of the present invention as a clear paint, the composition may be applied by the per se conventional method but, if desired, after application of a base coat to a substrate, it may be coated on the base coat in a wet-on-wet manner. The coating for the base coat may be water-based or solvent-based but where a
20 water-based coating is used, the base coat is preferably heated at 60 to 100°C for 2 to 10 minutes prior to application of the clear paint so that a more satisfactory finished film may be obtained.

25 The coating composition of the present invention can be applied to essentially all kinds of substrates, such as wood, metal, glass, cloth, plastics, foams, etc. or surfaces treated with a variety of primers. The coating composition of the present invention can be applied with particular advantage to plastic and metallic surfaces. Generally the
30 optimum film thickness varies with different uses but is preferably 20 to 100 μ m in many instances.

35 After application, the coat is cured. To attain a cured coating film of high crosslink density, curing is performed at 100 to 180°C and preferably at 120 to 160°C. The necessary cure time depends on curing temperature but may generally be

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1 10 to 30 minutes at 120 to 160°C .

The curable resin composition of the present invention can be used advantageously as a clear coating composition. As the base coating for use in this application, a color
5 pigment-containing water-based coating or a color pigment-containing organic solvent type coating is preferred. The preferred coating method is the two-coat one-bake method which comprises coating the curable resin composition of the present invention on a based coat which has not been cured as
10 yet and baking the two coats at a time.

However, when a water-based coating is used, the base coat is preferably heated at 60 to 100°C for 2 to 10 minutes prior to application of the clear coating in order to achieve an improved finished appearance. As the base coating, the
15 coatings disclosed in US Patent No. 5151125 and US Patent No. 5183504 can be utilized. Particularly the water-based coating composition described in Example 1 of US Patent No. 5183504 is most suitable in terms of finished appearance and performance characteristics.

20 When the curable resin composition of the present invention is used as a clear coating composition, a still more satisfactory coat can be obtained by a method which comprises coating a clear coating composition containing the curable resin composition of the present invention on the
25 surface of a base coat and further coating the clear coating composition containing the curable resin composition of the present invention in superimposition as a finish coat.

And further, because the coated film formed with the clear coating composition containing the curable resin
30 composition of the present invention shows an excellent adhesive property to the other coated film coated thereon, a peeling off between the coated film of the clear coating composition containing the curable resin composition of the present invention formed on the surface of previously coated
35 base coat film and the second base coat film superimposed onto

1 the said clear coat film hardly takes place. Hence, this
property makes it possible to recoat only the necessary part
of the product and therefor contribute to maintaining the
product quality and the saving of resources, among others.

5 Coating compositions containing the curable resin
composition of the present invention as a binder component
can be coated on various articles. The articles that can be
coated are virtually not limited only if the curable resin
composition can be heat-cured thereon. Thus, for example,
10 automotive bodies and car parts such as wheels and bumpers,
household electrical appliances such as air-conditioner
outdoor installations, and building materials such as
exterior sidings.

15 EXAMPLES

The following examples are further illustrative of the
present invention but by no means limitative of the scope of
the present invention.

Production Example 1

20 An acid anhydride group-containing polymer

A 3L reactor equipped with a thermometer, stirrer,
condenser, nitrogen inlet pipe and drip funnel was charged
with 700 parts by weight of xylene and 350 parts by weight of
Solvesso 100 and the temperature was increased to 130°C .
25 Using the drip funnel, a solution composed of 300 parts by
weight of styrene monomer, 109 parts by weight of 2-ethylhexyl
methacrylate, 325 parts by weight of isobutyl acrylate, 25.7
parts by weight of acrylic acid, 240 parts by weight of maleic
anhydride, 300 parts by weight of propyleneglycol monomethyl
30 ether acetate, 150 parts by weight of
t-butylperoxy-2-ethylhexanoate and 150 parts by weight of
xylene was fed dropwise to the reactor over a period of 3
hours. After completion of dropwise addition, the mixture was
maintained at 130°C for 30 minutes, at the end of which time
35 a solution composed of 20 parts by weight of

3 2

1 t-butylperoxy-2-ethylhexanoate and 20 parts by weight of
xylene was added dropwise over 30 minutes. After completion
of dropwise addition, the reaction was further continued at
130°C for one hour and the solvent was then distilled off
5 1100 parts by weight of the solvent to provide carboxyl
group- and carboxylic anhydride group-containing polymer
solution (a-1) with a nonvolatile content of 70% and a number
average molecular weight of 2000.

10 Production Example 2

A polymer containing free and esterified carboxyl groups

To 1590 parts by weight of the polymer solution (a-1)
obtained in Production Example 1 were added 125 parts by
weight of methanol and the reaction was conducted at 70°C for
15 23 hours to provide a polymer solution (A-1) containing free
and esterified carboxyl groups and having an acid value of 157.
The infrared absorption spectrum of this polymer solution
(A-1) was determined to confirm disappearance of acid
anhydride absorption (1785 cm^{-1}).

20

Production Example 3

An acid anhydride group-containing polymer

Using 870 parts by weight of xylene, 350 parts by weight
of Solvesso 100, 300 parts by weight of styrene monomer, 367
25 parts by weight of 2-ethylhexyl methacrylate, 113 parts by
weight of isobutyl acrylate, 220 parts by weight of maleic
anhydride, 300 parts by weight of propyleneglycol monomethyl
ether acetate, 170 parts by weight of
t-butylperoxy-2-ethylhexanoate, the procedure of Production
30 Example 1 was otherwise repeated to provide an acid anhydride
group-containing polymer solution (a-2) with a nonvolatile
content of 70% and a number average molecular weight of 2000.

Production Example 4

35 A polymer containing free and esterified carboxyl groups

3 3

1 To 1590 parts by weight of the polymer solution (a-2)
obtained in Production Example 3 were added 108 parts by
weight of methanol and the reaction was conducted at 70°C for
23 hours to provide a polymer solution (A-2) containing free
5 and esterified carboxyl groups and having an acid value of 126.
The infrared absorption spectrum of this polymer solution
(A-2) was determined to confirm disappearance of acid
anhydride absorption (1785 cm^{-1}).

10 Production Example 5

A polymer containing hydroxyl and epoxy groups

 A 3L reactor equipped with a thermometer, stirrer,
condenser, nitrogen gas inlet pipe and drip funnel was charged
with 700 parts by weight of xylene and 525 parts by weight of
15 propyleneglycol monomethyl ether acetate and the temperature
was increased to 130°C. Through the drip funnel, a solution
containing 200 parts by weight of Veova 9, 229 parts by
weight of glycidyl methacrylate, 231 parts by weight of
4-hydroxybutyl acrylate, 340 parts by weight of cyclohexyl
20 methacrylate, 120 parts by weight of
t-butylperoxy-2-ethylhexanoate, and 200 parts by weight of
xylene was dripped into the reactor over 3 hours. After
completion of dropwise addition, the reaction mixture was
maintained at 130°C for 30 minutes. Then, a solution
25 composed of 10 parts by weight of t-butylperoxy-2-
ethylhexanoate and 50 parts by weight of xylene was added
dropwise over 30 minutes. After completion of dropwise
addition, the reaction was further continued at 130°C for one
hour, at the end of which time 1200 parts by weight of the
30 solvent was distilled off to provide a polymer solution (B-1)
containing both hydroxyl and epoxy groups and having a
nonvolatile content of 77%, a number average molecular weight
of 1800, an epoxy equivalent of 625 and a hydroxyl equivalent
of 623.

1 Production Example 6

A polymer containing hydroxyl and epoxy groups

Using 950 parts by weight of xylene, 525 parts by weight of propyleneglycol monomethyl ether acetate, 233 parts by weight of VeoVa 9, 381 parts by weight of glycidyl methacrylate, 244 parts by weight of 4-hydroxybutyl acrylate, 142 parts by weight of isobutyl methacrylate and 120 parts by weight of t-butylperoxy-2-ethylhexanoate, the procedure of Production Example 5 was otherwise repeated and 1200 parts by weight of the solvent was removed to provide a polymer solution (B-2) containing hydroxyl and epoxy groups and having a nonvolatile content of 77%, a number average molecular weight of 1800, an epoxy equivalent of 376 and a hydroxyl equivalent of 591.

15

Production Example 7

A polymer containing hydroxyl and epoxy groups

Using 950 parts by weight of xylene, 525 parts by weight of propyleneglycol monomethyl ether acetate, 102 parts by weight of VeoVa 9, 545 parts by weight of 3,4-epoxycyclohexylmethyl methacrylate, 244 parts by weight of 4-hydroxybutyl acrylate, 62 parts by weight of isobutyl methacrylate and 121 parts by weight of t-butylperoxy-2-ethylhexanoate, the procedure of Production Example 5 was otherwise repeated and 1200 parts of the solvent was removed to provide a polymer solution (B-3) containing hydroxyl and epoxy groups and having a nonvolatile content of 77%, a number average molecular weight of 1800, an epoxy equivalent of 376, and a hydroxyl equivalent of 591.

30

A silicone polymer containing epoxy and/or alkoxy groups

A silicone polymer of general formula (II) wherein R¹, R² and R³ each represents methyl and R⁴ and R⁵ each represents that of methoxy/butoxy = 1/1, R⁶ represents that of methoxy/ γ -glycidoxypropyl = 1/1, q = 5, m = 4, n = 2 and having an

35

1 epoxy equivalent of 625 and an alkoxyl equivalent of 83
(manufactured by Mitsubishi Kasei Corporation, MKC Silicate
MSEP-HB2) was used as (C-1).

5 A silicone polymer of general formula (II) wherein R¹
and R² each represents methyl, R³, R⁴ and R⁵ each represents
methoxy, q = 7, m = 2, n = 0 and having an alkoxyl equivalent
of 81 (manufactured by Shin-Etsu Chemical Co., KC-89S) was
used as (C-2).

10 A silicone polymer of general formula (II) wherein R¹, R²,
R⁴ and R⁵ each represents methyl, R³ represents
 γ -glycidoxypropyl, q = 10, m = 2, n = 0 and having an epoxy
equivalent of 190 (manufactured by Nippon Unicar Co.,
F-244-05) was used as (C-3).

15 A silicone polymer of general formula (II) wherein R¹
represents methyl, R² represents that of
 γ -glycidoxypropyl/(trimethoxysilyl)ethyl = 2/1, R³, R⁴ and R⁵
each represents methyl, q = 6, m = 2, n = 0, and having an
epoxy equivalent of 318 and an alkoxyl equivalent of 213
(manufactured by Nippon Unicar Co., F-244-09) was used as
20 (C-4).

A silicone polymer of general formula (II) wherein R¹, R²,
R⁴ and R⁵ each represents methyl, R³ represents that of
 γ -glycidoxypropyl/phenethyl = 2/1, q = 6, m = 2, n = 0, and
having an epoxy equivalent of 297 (manufactured by Nippon
25 Unicar Co., F-244-06) was used as (C-5).

Production Example 8

A polyester resin

30 A reactor equipped with a thermometer, stirrer, condenser,
nitrogen gas inlet pipe, water separator and rectifying tube
was charged with 183 parts by weight of azelaic acid, 285
parts by weight of isophthalic acid, 221 parts by weight of
trimethylolpropane, 110 parts by weight of Cardura E
(manufactured by Shell) and 290 parts by weight of neopentyl
35 glycol and heated. After the mixture was melted to become

3 6

1 stirable, 0.2 parts by weight of dibutyltin oxide was supplied
to begin stirring, and the reactor temperature was increased
to 220°C at the constant elevation rate from 180 to 220°C for
3 hours. Water generated from the condensation was
5 evaporated to outside. After the temperature was increased
to 220°C, the reaction mixture was maintained at 220°C for 1
hour. Then, 30 parts by weight of xylene was added gradually
into the reactor as the reflux solvent to change the reaction
condition to the condensation under the existence of the
10 solvent, and continued the reaction. When the acid value of
the resin reached at the level of not more than 1, the
reaction mixture was cooled to 150°C and 238 parts by weight
of hexahydrophthalic anhydride was added dropwise into the
reaction mixture. After maintaining the heating to confirm
15 disappearance of acid anhydride absorption (1785 cm^{-1}) by
the determination of the infrared absorption spectrum of the
solution, the mixture was cooled to 100°C. After then, 383
parts by weight of xylene was added to provide a polyester
resin solution (D-1) having a nonvolatile content of 75%, a
20 number average molecular weight of 1100, an acid value of 70
(mgKOH/g) and a hydroxyl value of 200 (mgKOH/g).

Production Example 9

A polyester resin

25 Using 192 parts by weight of azelaic acid, 264 parts by
weight of isophthalic acid, 179 parts by weight of
trimethylolpropane, 110 parts by weight of Cardura E
(manufactured by Shell), 340 parts by weight of neopentyl
glycol, 0.2 parts by weight of dibutyltin oxide, 378 parts by
30 weight of hexahydrophthalic anhydride and 459 parts by weight
of xylene, the procedure of Production Example 8 was
otherwise repeated to provide a polyester resin solution
(D-2) having a nonvolatile content of 75%, a number average
molecular weight of 1100, an acid value of 150 (mgKOH/g), a
35 hydroxyl value of 150 (mgKOH/g).

1

Production Example 10

A polyester resin

Using 161 parts by weight of azelaic acid, 285 parts by
5 weight of isophthalic acid, 205 parts by weight of
trimethylolpropane, 110 parts by weight of Cardura E
(manufactured by Shell), 326 parts by weight of neopentyl
glycol, 0.2 parts by weight of dibutyltin oxide, 204 parts by
weight of hexahydrophthalic anhydride, 204 parts by weight of
10 trimellitic anhydride and 469 parts by weight of xylene, the
procedure of Production Example 8 was otherwise repeated to
provide a polyester resin solution (D-3) having a nonvolatile
content of 75%, a number average molecular weight of 1100, an
acid value of 130 (mgKOH/g), a hydroxyl value of 157 (mgKOH/g).

15

Production Example 11

A polyester resin

Using 155 parts by weight of azelaic acid, 273 parts by
weight of isophthalic acid, 251 parts by weight of
20 trimethylolpropane, 110 parts by weight of Cardura E
(manufactured by Shell), 295 parts by weight of neopentyl
glycol, 0.2 parts by weight of dibutyltin oxide, 278 parts by
weight of hexahydrophthalic anhydride, 278 parts by weight of
trimellitic anhydride and 519 parts by weight of xylene, the
25 procedure of Production Example 8 was otherwise repeated to
provide a polyester resin solution (D-4) having a nonvolatile
content of 75%, a number average molecular weight of 1100, an
acid value of 160 (mgKOH/g), a hydroxyl value of 132 (mgKOH/g).

30

Production Example 12

A polyester resin

Using 157 parts by weight of azelaic acid, 277 parts by
weight of isophthalic acid, 322 parts by weight of
trimethylolpropane, 110 parts by weight of Cardura E
35 (manufactured by Shell), 216 parts by weight of neopentyl

3 8

- 1 glycol, 0.2 parts by weight of dibutyltin oxide, 367 parts by weight of hexahydrophthalic anhydride and 456 parts by weight of xylene, the procedure of Production Example 8 was otherwise repeated to provide a polyester resin solution
- 5 (D-5) having a nonvolatile content of 75%, a number average molecular weight of 1100, an acid value of 95 (mgKOH/g), a hydroxyl value of 193 (mgKOH/g).

Production Example 13

10 A polyester resin

- Using 181 parts by weight of azelaic acid, 319 parts by weight of isophthalic acid, 282 parts by weight of trimethylolpropane, 110 parts by weight of Cardura E (manufactured by Shell), 204 parts by weight of neopentyl
- 15 glycol, 0.2 parts by weight of dibutyltin oxide, 192 parts by weight of trimellitic anhydride and 397 parts by weight of xylene, the procedure of Production Example 8 was otherwise repeated to provide a polyester resin solution
- (D-6) having a nonvolatile content of 75%, a number average
- 20 molecular weight of 2300, an acid value of 94 (mgKOH/g), a hydroxyl value of 200 (mgKOH/g).

Production Example 14

A polyester resin

- 25 A reactor equipped with a thermometer, stirrer, condenser, nitrogen gas inlet pipe, water separator and rectifying tube was charged with 258 parts by weight of hexahydrophthalic anhydride, 184 parts by weight of isophthalic acid, 213 parts by weight of trimethylolpropane, 180 parts by weight of
- 30 neopentyl glycol, 72 parts by weight of neopentyl glycol hydroxypivalate, 94 parts by weight of Cardura E (manufactured by Shell) and heated. After the mixture was melted to become stirable, 0.2 parts by weight of dibutyltin oxide was supplied to begin stirring, and the reactor temperature was
- 35 increased to 220°C at the constant elevation rate from 180

1 to 220°C for 3 hours. Water generated from the condensation
was evaporated to outside. After the temperature was
increased to 220°C, the reaction mixture was maintained at
220°C for 1 hour. Then, 17 parts by weight of xylene was
5 added gradually into the mixture as the reflux solvent to
proceed the reaction of condensation under the existence of
the solvent. When the acid value of the resin reached at
10.0, the reaction mixture was cooled to 150°C and 182 parts
by weight of Placel M (manufactured by Daicel Chemical
10 Industries) was added dropwise into the reaction mixture.
After maintaining the heating for 1 hour, the mixture was
cooled to 100°C. A 264 parts by weight of xylene was further
added to provide a polyester resin solution (D-7) having a
nonvolatile content of 79%, a number average molecular weight
15 of 1400, an acid value of 8.0 (mgKOH/g) and a hydroxyl value
of 210 (mgKOH/g).

Production Example 15

A polyester resin

20 Using 105 parts by weight of azelaic acid, 334 parts by
weight of hexahydrophthalic anhydride, 225 parts by weight of
trimethylolpropane, 100 parts by weight of Cardura E
(manufactured by Shell), 294 parts by weight of
3-methyl-1,5-pentanediol, 0.2 parts by weight of dibutyltin
25 oxide and 250 parts by weight of xylene, the procedure of
Production Example 14 was otherwise repeated to provide a
polyester resin solution (D-8) having a nonvolatile content of
70%, a number average molecular weight of 1200, an acid value
of 9.1 (mgKOH/g), a hydroxyl value of 290 (mgKOH/g).

30

Melamine resin

Cymel 327 (manufactured by Mitsui-Cytec Co.) was used as
(E-1).

35 Cymel 202 (manufactured by Mitsui-Cytec Co.) was used as
(E-2).

4 0

1 Super-Beckamine 13-548 (Dainippon Ink and Chemicals) was
used as (E-3).

Uvan 20N-60 (Mitsui Toatsu Chemicals) was used as (E-4).

Uvan 128 (Mitsui Toatsu Chemicals) was used as (E-5).

5 Curing catalyst

Tetrabutylammonium bromide was used as (F-1).

Tetrabutylammonium salicylate was used as (F-2).

Tetrabutylammonium glycolate was used as (F-3).

Tetrabutylammonium nitrate was used as (F-4).

10 Dibutyltin diacetate was used as (G-1).

Monobutyltin trioctoate was used as (G-2).

Dibutyltin didodecylbenzenesulfonate was used as (G-3).

Monobutyltin triacetate was used as (G-4).

Stabilizer

15 Triethyl orthoformate was used as (H-1).

Surface conditioner

Modaflow (manufactured by Monsanto) was used as (I-1).

Ultraviolet absorber

20 Tinuvin 900 (manufactured by Ciba-Geigy) was used as
(J-1).

Photostabilizer

Tinuvin 123 (manufactured by Ciba-Geigy) was used as
(K-1).

25 Preparation of a coated panel

A 0.8 mm-thick dull steel panel treated with zinc
phosphate was electrocoated with a cationic electrodeposition
paint (Power Top u-50, Nippon Paint Co.) in a dry thickness
of about 25 μ m. This electrocoating film was further air
30 spray-coated with an intermediate coating (Orga P-2
intermediate coat, manufactured by Nippon Paint Co.) in a dry
thickness of about 40 μ m, followed by 30-minute baking at
140°C.

Then, this coated panel was air spray-coated with an
35 acryl-melamine solvent type base paint A or an acryl-melamine

- 1 solvent type base paint B (both manufactured by Nippon Paint
Co.) in a dry thickness of about $16\mu\text{m}$ followed by about 7
minutes' setting. Where a water-based base coating
(manufactured by Nippon Paint Co.) was used, air spray-coating
5 was followed by about 1 minute of setting and 5 minutes'
preheating at 80°C .

The solvent type base coating A was prepared by
compounding 20 parts by weight of an acrylic resin (80%
solids, acid value = 30, OH value = 100, number average
10 molecular weight 1800), 30 parts by weight of a polyester
resin (80% solids, acid value = 12, OH value = 100, number
average molecular weight 2600), 40 parts by weight of Cymel
202 (Mitsui Cytec Co.) and 10 parts by weight of Cymel 327
(Mitsui Cytec Co.) for melamine resin, 10 parts by weight of
15 Alpaste 60-600 (Toyo Aluminum Co.) for pigment, and 7 parts by
weight of isopropyl alcohol.

The solvent type base coating B was prepared by
compounding 20 parts by weight of an acrylic resin (80%
solids, acid value = 30, OH value = 100, number average
20 molecular weight 1800), 30 parts by weight of a polyester
resin (70% solids, acid value = 12, OH value = 175, number
average molecular weight 1300), 40 parts by weight of Cymel
202 (Mitsui Cytec Co.) and 10 parts by weight of Cymel 327
(Mitsui Cytec Co.) for melamine resin, 10 parts by weight of
25 Alpaste 60-600 (Toyo Aluminum Co.) for pigment, and 7 parts by
weight of isopropyl alcohol.

The water-based base coating was prepared by formulating
56 parts by weight of aqueous acrylic resin (50% solids, acid
value = 58, OH value = 70, number average molecular weight =
30 12000), 15 parts of Cymel 303 (Mitsui Cytec Co.), 21.5 parts
by weight of urethane emulsion (33% solids, acid value =
16.2), 7.5 parts by weight of Alpaste 7160N (Toyo Aluminum
Co.) for pigment, and 1 part by weight of isostearyl
phosphate for stabilizer.

35 Coating with the coating composition of the invention

1 Coating compositions of the solid compositions shown in
Tables 1 to 6 were respectively adjusted to a Ford cup No. 4
viscosity of 30 seconds and using an electrostatic coating
machine, Auto REA (Randsburg-Gema), each was coated at a
5 spray pressure of 5 kg/cm² in a dry film thickness of about
40 μ m and after about 7 minutes of setting, baked at 140°C for
25 minutes. In tables 1 to 4, the solvent type base coating
A was used. In tables 5 and 6, the solvent type base coating
B was used.

10 Evaluation of coating film characteristics

1. SVS (nonvolatile matter)

After the viscosities of the coatings were uniformly
adjusted to a Ford cup No. 4 viscosity of 30 seconds/20°C,
0.5 g was accurately taken from each coating, diluted with
15 3 cc of toluene, baked at 110°C for one hour, and the
nonvolatile matter (weight) was determined and converted to
volume. The results are shown in Tables 1 to 6.

2. Pencil hardness

Determined according to JIS K 5400, 8.4.2. The results
20 are shown in Tables 1 to 6.

3. Water resistance

Each coated panel was immersed in tap water at 40°C and
allowed to stand for 10 days. Thereafter, the coating film
of the coated panel was visually inspected. Evaluation was
25 made according to the following criteria. The results are
shown in Tables 1 to 6.

○: No abnormality

△: Slight film abnormality

×: Overt film abnormality

30 4. Mar resistance

A 2×2 cm flannel cloth coated with 1 g of 50% aqueous
dispersion of cleanser (New Homing Cleanser, Kao Corporation)
was mounted on a Gakushin-type color friction fastness tester
(manufactured by Daiei Kagaku Seiki). Under a load of 500 g,
35 the sliding head was reciprocated for 20 cycles and the 20°

4 3

- 1 gloss of the test area was determined to calculate the gloss retention. The results are shown in Tables 1 to 6.

◎ : gloss retention $\geq 85\%$

○ : gloss retention $\geq 70\%$ to $<85\%$

- 5 △ : gloss retention $\geq 40\%$ to $<70\%$

× : gloss retention $<40\%$

5. Acid resistance

- The specimen was contacted with 0.5 cc of 1 wt. % aqueous solution of sulfuric acid at 75°C for 30 minutes and the surface of the coat was visually inspected and evaluated according to the following criteria. The results are shown in Tables 1 to 6.

◎ : No abnormality

○ : Small traces

- 15 △ : Large traces

× : Film abnormalities found

6. Storage stability

- After the viscosities of the coatings according to the solid compositions shown in Tables 1 to 4 were uniformly adjusted to a Ford cup No. 4 viscosity of 30 seconds/20°C, the coatings were stored for 10 days at 40°C. After that, the viscosity changes (seconds) were measured by Ford cup No.4 method at 20°C. The results are shown in Tables 1 to 4.

7. NSR-ability

- 25 An intermediate-coated panel prepared by the procedure described under Preparation of a coated panel was coated, by the air spray method, with an acryl-melamine series solvent-type base coating (manufactured by Nippon Paint) in a dry film thickness of about 16 μ m and the coat was set for about 7 minutes. Where the water-based base coating (manufactured by Nippon Paint) was used, air spray coating was followed by about 1 minute's setting and, then, the coat was preheated at 80°C or 5 minutes.

- 35 Then, the coatings according to the solid compositions shown in Tables 1 to 6 were respectively adjusted to a Ford

1 cup No. 4 viscosity of 30 seconds and applied using the
electrostatic coating machine Auto REA (Randsburg-Gema) at a
spray pressure of 5 kg/cm² in a dry film thickness of about
40 μ m and, after about 7 minutes of setting, baked at 160°C
5 for 60 minutes.

Immediately after baking, each coated panel was placed
and allowed to stand in a desiccator for 30 minutes. Then,
the acryl-melamine solvent-type base coating (manufactured by
Nippon Paint) was applied, by the air spray method, in a dry
10 film thickness of about 16 μ m and set for about 7 minutes.
When the water-based coating (manufactured by Nippon Paint)
was used, air spray coating was followed by about 1 minute of
setting and the coat was preheated at 80°C for 5 minutes.

Then, the coatings according to the solid compositions
15 shown in Tables 1 to 6 were respectively adjusted to a Ford
cup No. 4 viscosity of 30 seconds and coated using the
electrostatic coating machine Auto REA (Randsburg-Gema) at a
spray pressure of 5 kg/cm² in a dry film thickness of about
40 μ m and, after about 7 minutes of setting, baked at 120°C
20 for 30 minutes to provide coated panels.

Using the type A cutting edge of the NT cutter
(trademark) model S as held at an angle of about 30° with the
coated surface of the coated panel, the coated side of the
coated panel was scored with 100 (10×10) crosshatches (2 mm
25 across) reaching the base and a 24 mm-wide cellophane
adhesive tape (manufactured by Nichiban) was laid over and
stuck evenly to the coated surface using care not to leave air
bubbles on the crosshatches. Immediately then, holding one
end of the tape, the tape was quickly pulled off in a
30 direction perpendicular to the coated surface and the
evaluation was made according to the following criteria. The
results are shown in Tables 1 to 6.

◎ : Peeled area rate 0%

○ : Peeled area rate <5%; no completely peeled square

35 □ : Peeled area rate <15%; no completely peeled square

4 5

1

Δ : Peeled area rate $< 35\%$

\times : Peeled area rate $\geq 35\%$

5

Table 1

	Examples											
	1	2	3	4	5	6	7	8	9	10	11	12
Polymer A-1	23.4	21.0	18.6	16.2	21.4	21.5	41.7	33.7	25.7	17.8	30.9	28.0
Polymer A-2	--	--	--	--	--	--	--	--	--	--	--	--
Polymer B-1	46.6	49.0	51.4	53.8	48.6	48.5	--	--	--	--	--	--
Polymer B-2	--	--	--	--	--	--	38.3	36.3	34.3	32.2	39.1	42.0
Polymer B-3	--	--	--	--	--	--	--	--	--	--	--	--
Polymer C-1	10.0	10.0	10.0	10.0	10.0	10.0	--	--	--	--	10.0	10.0
Polymer C-2	--	--	--	--	--	--	--	--	--	--	--	--
Polymer C-3	--	--	--	--	--	--	--	--	--	--	--	--
Polymer C-4	--	--	--	--	--	--	10.0	10.0	10.0	10.0	--	--
Polymer C-5	--	--	--	--	--	--	--	--	--	--	--	--
Polymer D-1	20.0	--	--	--	--	--	--	--	--	--	--	--
Polymer D-2	--	20.0	--	--	--	--	--	--	--	--	--	--
Polymer D-3	--	--	20.0	--	--	--	--	--	--	--	--	--
Polymer D-4	--	--	--	20.0	--	--	10.0	20.0	30.0	40.0	20.0	20.0
Polymer D-5	--	--	--	--	20.0	20.0	--	--	--	--	--	--
Polymer D-6	--	--	--	--	--	--	--	--	--	--	--	--
E-1	--	--	--	--	--	--	--	--	--	--	--	--
E-2	--	--	--	--	--	--	--	--	--	--	--	--
E-3	--	--	--	--	--	--	--	--	--	--	--	--
E-4	--	--	--	--	--	--	--	--	--	--	--	--
F-1	1.0	1.0	1.0	1.0	1.0	1.0	--	--	--	--	--	--
F-2	--	--	--	--	--	--	--	--	--	--	1.0	1.0
F-3	--	--	--	--	--	--	1.0	1.0	1.0	1.0	--	--
F-4	--	--	--	--	--	--	--	--	--	--	--	--
G-1	--	--	--	--	--	--	--	--	--	--	--	--
G-2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
G-3	--	--	--	--	--	--	--	--	--	--	--	--
G-4	--	--	--	--	--	--	--	--	--	--	--	--
H-1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
I-1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
J-1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
K-1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Base coating	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type
SVS	51.5	52.1	51.5	51.7	51.5	50.4	50.0	50.1	50.3	50.5	50.4	51.3
Pencil hardness	F	F	F	F	F	H	2H	H	H	F	F	F
Water resistance	○	○	○	○	○	○	○	○	○	○	○	○
Mar resistance	○	○	○	○	○	○	○	○	○	○	○	○
Acid resistance	○	○	○	○	○	○	○	○	○	○	○	○
Storage stability	○	○	○	○	○	○	○	○	○	○	○	○
NSR-ability	◎	○	○	○	◎	○	○	◎	◎	◎	◎	◎

Table 4

Examples		Comparative Examples							
	37	38	1	2	3	4	5	6	7
Polymer A-1	37.8	28.4	50.5	48.8	52.7	15.0	22.2	50.5	
Polymer A-2	--	--	--	--	--	--	--	--	
Polymer B-1	22.2	31.6	--	--	--	--	--	--	
Polymer B-2	--	--	29.5	51.2	--	5.0	37.8	9.5	
Polymer B-3	--	--	--	--	--	--	--	--	
Polymer C-1	--	--	--	--	--	--	--	--	
Polymer C-2	--	--	--	--	--	--	--	--	
Polymer C-3	--	--	--	--	--	--	--	--	
Polymer C-4	--	--	--	--	47.3	20.0	20.0	20.0	
Polymer C-5	20.0	20.0	20.0	--	--	--	--	--	
Polymer D-1	--	--	--	--	--	--	--	--	
Polymer D-2	--	--	--	--	--	--	--	--	
Polymer D-3	--	--	--	--	--	--	--	--	
Polymer D-4	--	--	--	--	--	--	--	--	
Polymer D-5	20.0	20.0	--	--	--	20.0	20.0	20.0	Commercial melamine-containing high-solid coating composition
Polymer D-6	--	--	--	--	--	40.0	--	--	
E-1	--	--	--	--	--	--	--	--	
E-2	--	--	--	--	--	--	--	--	
E-3	--	--	--	--	--	--	--	--	
E-4	--	--	--	--	--	--	--	--	
F-1	--	--	--	--	--	--	--	--	
F-2	--	--	--	--	--	--	--	--	
F-3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
F-4	--	--	--	--	--	--	--	--	
G-1	--	--	--	--	--	--	--	--	
G-2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
G-3	--	--	--	--	--	--	--	--	
G-4	--	--	--	--	--	--	--	--	
H-1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
I-1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
J-1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
K-1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Base coating	solvent type	Water-based	Solvent type	Solvent type	Solvent type	Solvent type	Solvent type	Solvent type	solvent type
SVS	52.7	53.4	52.6	43.3	66.5	52.8	52.0	50.5	53.5
Pencil hardness	H	F	F	F	2B	2H	B	B	F
Water resistance	○	○	○	△	○	○	○	○	○
Mar resistance	○	○	○	○	○	○	○	△	○
Acid resistance	◎	○	◎	○	○	△	△	○	x
Storage stability	14	17	28	24	17	31	12	11	13
NSR-ability	○	○	x	x	△	△	○	△	◎

Commercial
melamine-
containing
high-solid
coating
composition

Table 6

	Examples								Comparative Examples							
	13	14	15	16	1	2	3	4	5	6	7					
Polymer A-1	30.8	37.2	28.8	27.3	25.2	36.1	27.3	7.3	22.5	47.7						
Polymer A-2	--	--	--	--	--	--	--	--	--	--						
Polymer B-1	34.2	22.8	31.2	37.7	14.8	33.9	47.7	12.7	37.5	12.3						
Polymer B-2	--	--	--	--	--	--	--	--	--	--						
Polymer C-1	--	--	--	10.0	--	--	--	--	--	--						
Polymer C-2	--	--	--	--	--	--	--	--	--	--						
Polymer C-3	--	--	--	--	--	--	--	--	--	--						
Polymer C-4	10.0	15.0	15.0	--	15.0	15.0	--	55.0	15.0	15.0						
Polymer D-7	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0						
Polymer D-8	--	--	--	--	--	--	--	--	--	--						
E-1	--	10.0	10.0	--	--	--	--	--	--	--						
E-2	10.0	--	--	10.0	30.0	--	10.0	10.0	10.0	10.0						
E-5	--	--	--	--	--	--	--	--	--	--						
F-1	--	--	--	--	--	--	--	--	--	--						
F-2	--	--	--	--	--	--	--	--	--	--						
F-3	1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0						
G-1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0						
G-2	--	--	--	--	--	--	--	--	--	--						
H-1	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5						
J-1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0						
K-1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0						
Base coating	solvent type	solvent type	solvent type	Water-based	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type	solvent type
SVS	52.1	52.7	53.6	51.5	51.3	52.9	47.9	63.5	53.4	51.3	51.3					
Pencil hardness	H	F	F	H	2H	HB	H	B	B	2B	F					
Water resistance	○	○	○	○	○	△	○	×	○	△	○					
Mar resistance	○	○	○	○	○	△	△	○	△	△	△					
Acid resistance	○	○	○	○	×	○	○	×	○	△	△					
NSR-ability	○	○	○	○	×	○	○	×	△	○	○					

5 2

1 INDUSTRIAL APPLICABILITY

5 The curable resin composition of this invention provides for a coating film having a high quality appearance, high acid resistance, mar resistance and further an excellent adhesive property and also can be provided with a high-solid feature. The coating composition obtainable with the curable resin composition of this invention can be provided with an excellent NSR-ability and can be advantageously used for automotive parts and exterior building materials, among other

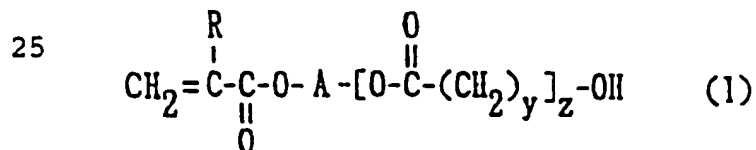
10 uses.

C L A I M S

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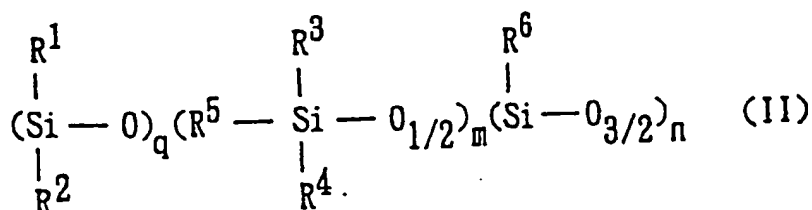
1. A curable resin composition comprising
 5 to 70 weight % of a polymer containing free and
 5 esterified carboxyl groups and having an acid value of 50 to
 300 (mgKOH/g) and a number average molecular weight of 1500 to
 8000 (1e) as obtainable by reacting an acid anhydride group-
 containing polymer (1c), which is obtainable by
 10 copolymerizing 10 to 40 weight % of an acid anhydride group-
 containing ethylenically unsaturated monomer (1a) with 90 to
 60 weight % of a copolymerizable other ethylenically
 unsaturated monomer (1b), with a monohydric alcohol of 1 to
 12 carbon atoms (1d) in the ratio (the number of mols of acid
 anhydride group in acid anhydride-containing polymer (1c)) /
 15 (the number of mols of hydroxyl group in monohydric alcohol
 (1d)) of 1/10 to 1/1,

1 to 70 weight % of a hydroxyl group- and epoxy group-
 containing polymer having an epoxy equivalent of 200 to 1000,
 a hydroxyl equivalent of 250 to 1500 and a number average
 20 molecular weight of 1500 to 8000 (2d) as obtainable by
 copolymerizing 5 to 60 weight % of a hydroxylalkyl
 (meth)acrylate monomer (2a) of the general formula (I):



(wherein R represents hydrogen or methyl; A represents a
 30 straight-chain or branched alkylene group of 2 to 8 carbon
 atoms; y represents a whole number of 3 to 7; z represents a
 whole number of 0 to 4) with 10 to 60 weight % of an epoxy
 group-containing ethylenically unsaturated monomer
 (2b) and 0 to 85 weight % of an ethylenically unsaturated
 35 monomer (2c) copolymerizable therewith,

1 to 45 weight % of an epoxy group- and/or alkoxy group-containing silicone polymer having an alkoxy equivalent of 50 to 1500 and an epoxy equivalent of 100 to 1500 (3a) of the general formula (II):



(wherein R¹, R², R³, R⁴, R⁵, and R⁶ are the same or different and each represents alkyl of 1 to 10 carbon atoms, phenyl, phenethyl, alkoxy of 1 to 5 carbon atoms, R'-Si(OR'), R'-Si(OR'), CH₃, R'-Si(OR')(CH₃), or R'-Y; R' represents a straight-chain or branched alkylene group which may have an ether bond and/or an ester bond; R' represents alkyl of 1 to 5 carbon atoms; Y represents an epoxy group-containing acyclic or cyclic hydrocarbon residue; q represents a whole number of 1 to 20, m represents a whole number of 0 to 4, n represents a whole number of 0 to 2; the order of the parenthesized groups occurring in q, m and n repetitions is random and not restricted to the formula shown), and

1 to 70 weight % of a polyester resin having a hydroxyl value of not greater than 300 (mgKOH/g), an acid value of 30 to 400 (mgKOH/g) and a number average molecular weight of 400 to 6000 (4a).

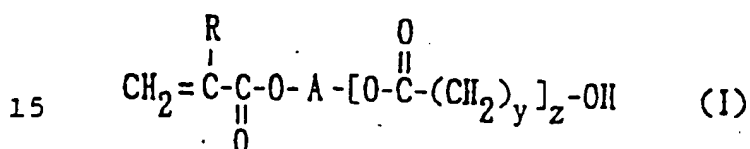
2. A curable resin composition comprising

5 to 70 weight % of a polymer containing free and esterified carboxyl groups and having an acid value of 50 to 300 (mgKOH/g) and a number average molecular weight of 1500 to 8000 (1e) as obtainable by reacting an acid anhydride group-containing polymer (1c), which is obtainable by copolymerizing 10 to 40 weight % of an acid anhydride group-containing ethylenically unsaturated monomer (1a) with 90 to 60 weight % of a copolymerizable other ethylenically

5 5

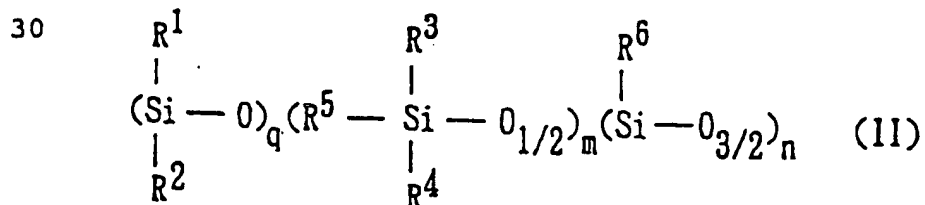
1 unsaturated monomer (1b), with a monohydric alcohol of 1 to
 12 carbon atoms (1d) in the ratio (the number of mols of acid
 anhydride group in acid anhydride-containing polymer (1c)) /
 (the number of mols of hydroxyl group in monohydric alcohol
 5 (1d)) of 1/10 to 1/1,

1 to 70 weight % of a hydroxyl group- and epoxy group-
 containing polymer having an epoxy equivalent of 200 to 1000,
 a hydroxyl equivalent of 250 to 1500 and a number average
 molecular weight of 1500 to 8000 (2d) as obtainable by
 10 copolymerizing 5 to 60 weight % of a hydroxylalkyl
 (meth)acrylate monomer (2a) of the general formula (I):



(wherein R represents hydrogen or methyl; A represents a
 straight-chain or branched alkylene group of 2 to 8 carbon
 20 atoms; y represents a whole number of 3 to 7; z represents a
 whole number of 0 to 4) with 10 to 60 weight % of an epoxy
 group-containing ethylenically unsaturated monomer
 (2b) and 0 to 85 weight % of an ethylenically unsaturated
 monomer (2c) copolymerizable therewith,

25 1 to 50 weight % of an epoxy group- and/or alkoxyl group-
 containing silicone polymer having an alkoxyl equivalent of 50
 to 1500 and an epoxy equivalent of 100 to 1500 (3a) of the
 general formula (II):



35 (wherein R¹, R², R³, R⁴, R⁵, and R⁶ are the same or different

5 6

1 and each represents alkyl of 1 to 10 carbon atoms, phenyl,
phenethyl, alkoxy of 1 to 5 carbon atoms, $R'-Si(OR')$,
 $R'-Si(OR'),CH_2$, $R'-Si(OR')(CH_2)_2$, or $R'-Y$; R' represents a
5 ether bond and/or an ester bond; R' represents alkyl of 1 to
5 carbon atoms; Y represents an epoxy group-containing acyclic
or cyclic hydrocarbon residue; q represents a whole number of
1 to 20, m represents a whole number of 0 to 4, n represents
a whole number of 0 to 2; the order of the parenthesized
10 groups occurring in q , m and n repetitions is random and not
restricted to the formula shown),

1 to 60 weight % of a polyester resin having a hydroxyl
value of 50 to 400 (mgKOH/g), an acid value of not greater
than 30 (mgKOH/g) and a number average molecular weight of 400
15 to 6000 (5a), and

1 to 40 weight % of an aminoplast curing agent (6a).

3. The curable resin composition according to claim 1
wherein the molar ratio of the carboxyl group contained in
said polymer containing free and esterified carboxyl groups
20 (1e) and said polyester resin (4a) to the epoxy group
contained in said hydroxyl group- and epoxy group-containing
polymer (2d) and said epoxy group- and/or alkoxy group-
containing silicone polymer (3a) is (carboxyl group) / (epoxy
group) ratio = 1/1.6 to 1/0.6.

25 4. The curable resin composition according to claim 2
wherein the molar ratio of the carboxyl group contained in
said polymer containing free and esterified carboxyl groups
(1e) and said polyester resin (5a) to the epoxy group
contained in said hydroxyl group- and epoxy group-containing
30 polymer (2d) and the epoxy group contained in said epoxy
group- and/or alkoxy group-containing silicone polymer (3a)
is (carboxyl group) / (epoxy group) ratio = 1/1.6 to 1/0.6.

5. The curable resin composition according to claim 1, 2,
3 or 4 wherein said copolymerizable other ethylenically
35 unsaturated monomer (1b) is a carboxyl group-containing

1 monomer (1b²).

6. The curable resin composition according to claim 1, 2,
3 or 4 wherein said acid anhydride group-containing polymer
(1c) contains at least two acid anhydride groups on the
5 average per molecule.

7. The curable resin composition according to claim 2 or
4 wherein the weight ratio of said polyester resin (5a) to
said aminoplast curing agent (6a) is 9/1 to 4/6.

8. The curable resin composition according to claim 2 or
10 4 wherein the weight ratio of the total amount of said
polyester resin (5a) and said aminoplast curing agent (6a) to
the total amount of said polymer containing free and
esterified carboxyl groups (1e), said hydroxyl group- and
epoxy group-containing polymer (2d) and said epoxy group-
15 and/or alkoxyl group-containing silicone polymer (3a) is 5/95
to 7/3.

9. The curable resin composition according to claim 1
which contains an aminoplast curing agent.

10. The curable resin composition according to claim 1 or
20 2 which contains a quaternary ammonium salt catalyst.

11. The curable resin composition according to claim 1 or
2 which contains an organotin compound.

12. The curable resin composition according to claim 1 or
2 which contains a hydrolyzable ester solvent.

25 13. A coating composition characterized in that it
contains the curable resin composition of claim 1 or 2 as a
binder component.

14. A method of producing a coating film characterized in
that it comprises (A), (B), (C) and (D), viz. (A) a step of
30 forming an undercoat layer, and an intermediate coating layer
where necessary, on a substrate, (B) a step of coating a
water-based or solvent-type base coating on the coating layer
formed in step (A), (C) a step of coating the coating
composition of claim 13 in superimposition prior to curing of
35 said base coating or after curing of said base coating, and

5 8

- 1 (D) a step of causing said base coating and said coating
composition of claim 13 to cure or only said coating
composition of claim 13 to cure.

15. A coated article characterized in that it has a
5 coating layer formed from the coating composition of claim 13.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/JP 95/00757

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D133/14 C09D135/00 C09D183/04 C09D167/00 B05D7/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 252 558 (NIPPON PAINT CO. LTD.) 12 August 1992 see page 31, line 3 - line 9 ---	1
A	CA,A,2 105 753 (NIPPON PAINT CO. LTD.) 10 March 1994 see claim 1 -----	1

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Date of the actual completion of the international search

28 July 1995

Date of mailing of the international search report

30. 08. 95

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Schueler, D

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/JP 95/00757

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 2058364	29-06-92
		US-A- 5374682	20-12-94

CA-A-2105753	10-03-94	AU-B- 4613893	17-03-94
		EP-A- 0588560	23-03-94
		JP-A- 6166741	14-06-94
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